no metal-insulator transition at $T=41$ K.[10]

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[a]Permanent address: H. C. Ørsted Institute, Universitetsparken 5, DK-2100 Copenhagen, Denmark.

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Observation of Ultrasonic Anomaly near a Smectic-*A* – Smectic-*C* Phase Transition

S. Bhattacharya
The James Franck Institute, University of Chicago, Chicago, Illinois 60637

and

B. Y. Cheng
Institute for Physics, Academia Sincia, Beijing, The People's Republic of China

and

Bimal K. Sarma and J. B. Ketterson
Department of Physics and Astronomy and Materials Research Center, Northwestern University, Evanston, Illinois 60201

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The first observation is reported of an anomalous attenuation and velocity dispersion near a smectic-*A*–smectic-*C* phase transition in a liquid crystal. The anomaly is found to be strongly anisotropic and dominated by the Landau-Khalatnikov relaxation of the order parameter in contrast with other liquid-crystalline phase transitions.

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Possible second-order phase transitions in liquid crystals, nematic to smectic-*A* (*N*-*A*) and smectic-*A* to smectic-*C* (*A*-*C*), were proposed by de Gennes[1,2] in analogy with superfluid ^{4}He ($n=2$, $d=3$ universality class). Of the two the latter has received much less attention, though unlike the former[3] no controversy surrounds the second-order nature of the *A*-*C* transition. In this Letter we present the first experimental evidence of the existence of anomalies in both the attenuation and the velocity dispersion of longitudinal ultrasound near the *A*-*C* phase transition.[4,5]

The Ginzburg-Landau free energy for the *A*-*C* transition can be written as[6]

$$\delta F \equiv F - F_0 = A|\psi|^2 + B|\psi|^4 + D|\nabla\psi|^2 + \ldots, \qquad (1)$$

where ψ is the complex order parameter, $\psi = \psi_0 e^{i\varphi}$ with ψ_0 the tilt angle of the molecular orientations from the layer normal and φ the azimuth. Above the transition temperature T_{AC}, $\langle\psi_0\rangle$ is identically zero, while below T_{AC} it grows continuously. The transition is driven by A (which is proportional to the elastic modulus keeping the molecules normal to the layer) going to zero. A recent x-ray scattering study[6] has shown that the growth of ψ_0 is essentially mean-field-like and an appropriate "Ginzburg criterion"[7] has been proposed.

In the smectic-A phase the velocity and the attenuation of longitudinal ultrasound is given by[8,9]

$$V^2(\theta)=\left(\frac{\partial P}{\partial \rho}\right)_{s,x}-2\left(\frac{\partial \varphi_3}{\partial \rho}\right)\cos^2\theta+\left(\frac{\partial \varphi_3}{\partial \nabla_3 u}\right)\cos^4\theta, \tag{2}$$

$$\alpha(\theta)=(\omega^2/2\rho v^3)[(2\nu_1+\nu_2+\nu_4+2\nu_5)\cos^2\theta+(\nu_2+\nu_4)\sin^2\theta-\tfrac{1}{2}(\nu_1+\nu_2-2\nu_3)\sin^2 2\theta], \tag{3}$$

where θ is the angle between the layer normal and the sound wave vector. In the presence of slow relaxation processes, additional contributions appear in the attenuation and the velocity becomes frequency dependent. They are given by

$$V(\omega)=V(0)\left(1+\frac{V(\infty)-V(0)}{V(0)}\frac{\omega^2\tau^2}{1+\omega^2\tau^2}\right), \tag{4}$$

$$\alpha_c(\omega)=\frac{V(\infty)-V(0)}{V^2(0)}\frac{\omega^2\tau}{1+\omega^2\tau^2}. \tag{5}$$

Near a second-order phase transition, the critical slowing down of order-parameter fluctuations given by a relaxation time τ causes anomalous damping and dispersion of sound. The quantity $[V(\infty)-V(0)]/V(0)$, known as the relaxation strength, represents the coupling between the sound wave and the relaxing variable, which is the order parameter in this case.

The material studied was 4-n-pentylphenyl thiol-4-n'-octyloxybenzoate ($\overline{8}$S5) which has a T_{AC} of 55.7 °C. A detailed x-ray scattering study[6] and an ac microcalorimetry study[10] have been performed on this material. The multiple-path sonic cell and the pulsed heterodyne rf spectrometer used in the experiment are described elsewhere.[11] The sample was cooled from the nematic phase where the alignment was obtained by a magnetic field of 20 kG and the field was left on during the measurements.[12] The multiple-path sonic cell and the rf spectrometer allowed us to perform measurements simultaneously for two mutually orthogonal directions of sound propagation and at several frequencies.

Figure 1 shows the temperature dependence of the sound velocity at 2, 6, and 10 MHz for three values of the angle θ between the sound wave vector and the smectic-A layer normal. For $\theta=90°$, there is little enhancement of the velocity dispersion; for $\theta=30°$, the enhancement is clearly visible; and at $\theta=0°$ it is substantially larger. We note that neither any enhancement of the velocity dispersion nor any unusual temperature dependence of the velocity occurs above T_{AC}. This is in strong contrast with other liquid-crystalline phase transitions[4] and notably with the N-A transition.[5]

If the enhancement of the dispersion is caused by a relaxation process, then from Eqs. (4) and (5) an excess attentuation is expected. Figure 2 shows the temperature dependence of the relative attenuation at 2 MHz for $\theta=0°$; it is barely visible at $\theta=90°$. We note again that in contrast with other phase transitions[4,5] (1) no pretransitional rise is seen above T_{AC} and (2) the anomaly is dominantly anisotropic. *Together, these data*

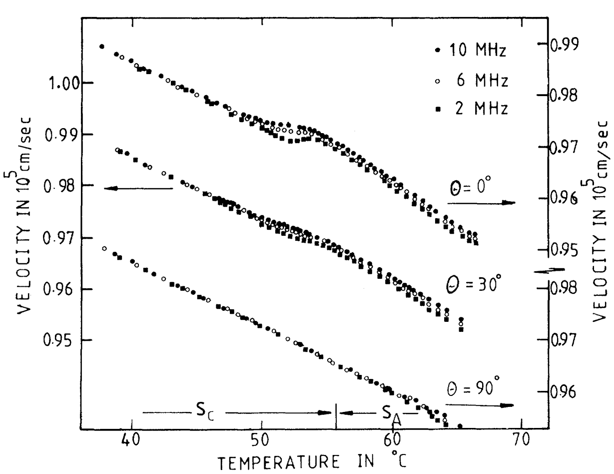

FIG. 1. Temperature dependence of the sound velocity at three frequencies for three angles: $\theta=0°$, 30°, and 90°.

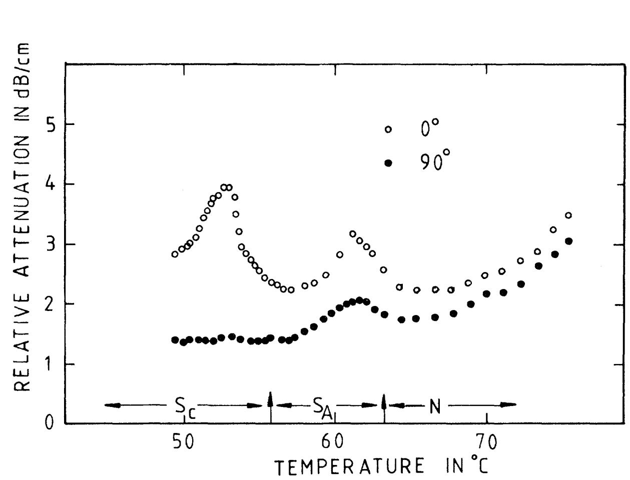

FIG. 2. Temperature dependence of the relative attenuation at 2 MHz for $\theta=0°$ and 90°.

demonstrate the existence of a dominantly anisotropic relaxational anomaly which is present only below T_{AC}.

In order to test the nature of this relaxation process, the frequency dependence of the anomalous attenuation was studied, as shown in Fig. 3. For all frequencies the anomaly is entirely below T_{AC}. The height of the peak above any reasonable background estimate departs markedly from the hydrodynamic ω^2 scaling; it is more nearly linear in ω as expected from Eq. (5). Furthermore, the position of the peak (corresponding to $\omega\tau = 1$)[13] shifts closer to T_{AC} at lower frequencies, thereby demonstrating a strong temperature dependence of τ, the relaxation time, which increases as T_{AC} is approached from below. The anomalous part thus becomes small deep in the C phase since τ is small and again near T_{AC} since τ is very large, as can be seen from Eq. (5).

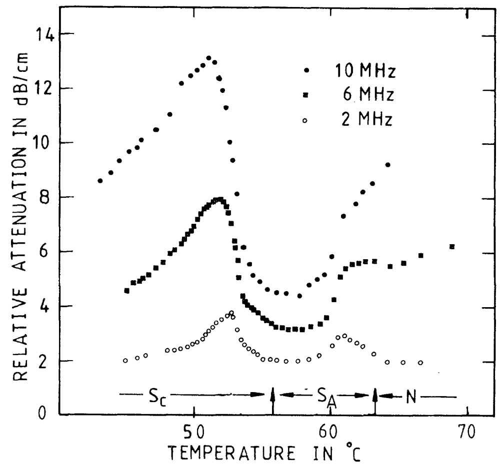

FIG. 3. Temperature dependence of the relative attenuation for $\theta = 0°$, at 2, 6, and 10 MHz. The data for various frequencies are shifted arbitrarily for clarity.

To the best of our knowledge no complete theoretical treatment of this problem exists. On the basis of our preliminary observations,[14] Andereck and Swift[15] have performed a mode-coupling calculation above T_{AC} of the anomaly due to the critical fluctuations. For details we refer to the original paper. They find that the anomalies for $\theta = 0°$ and $\theta = 90°$ are given by

$$\alpha(90°) = \left(\frac{\partial P}{\partial \rho}\right)_{\nabla_3 u}^{-1/2} \left(\frac{\partial A}{\partial \rho}\right)_{\nabla_3 u}^{2} \frac{k^2}{\gamma} \int \frac{d^3q}{(2\pi)^3} \frac{\chi(\vec{q})}{\omega^2 + 4\Gamma^2(\vec{q})} \tag{6}$$

and

$$\alpha(0°) = \left[\left(\frac{\partial P}{\partial \rho}\right)_{\nabla_3 u} + \left(\frac{\partial \varphi_3}{\partial \nabla_3 u}\right)_{\rho} - 2\left(\frac{\partial \varphi_3}{\partial \rho}\right)_{\nabla_3 u}\right]^{-1/2} \left[\left(\frac{\partial A}{\partial \rho}\right)_{\nabla_3 u} - \left(\frac{\partial A}{\partial \nabla_3 u}\right)_{\rho}\right]^{2} \frac{k^2}{\gamma} \int \frac{d^3q}{(2\pi)^3} \frac{\chi(\vec{q})}{\omega^2 + \Gamma^2(\vec{q})} . \tag{7}$$

The terms within the brackets in Eq. (7) have opposite signs since T_{AC} increases with decreasing $\nabla_3 u$, the gradient of the layer spacing,[16] and increases with increasing ρ, the density. Thus $\alpha(0°)$ is greater than $\alpha(90°)$. In other words, the relaxation strength is anisotropic depending upon the sensitiveness of T_{AC} on the smectic layer spacing.

While the anisotropic relaxation strength is correctly explained by this theory, no anomaly is seen above T_{AC} as would be expected from the critical fluctuations. Since the anomaly is dominated by effects that manifest themselves below T_{AC} the coupling must exist between the bulk order parameter and the sound mode. The qualitative behavior of the effect (i.e., the presence of a relaxation and the increase in the relaxation time τ as T_{AC} is approached from below) is consistent with the conventional Landau-Khalatnikov relaxation of the bulk order parameter.[17,18] The relaxation time τ is then given by[19] $\tau^{-1} \propto A/\eta$, where η is a kinetic coefficient. τ has a temperature dependence of the form $(T_C - T)^{-1}$ in the mean-field theory.

Quantitative data analysis has proved extremely difficult because of the proximity of the N-A transition. This prevents an unambiguous assignment of the background at higher frequencies as can be seen in Fig. 3. Furthermore, below T_{AC} the system is multidomained even in the presence of a magnetic field and a proper averaging over the domains is necessary.[20] These problems prevent an exhaustive data analysis at this stage. We have also noticed a rapid decrease in the velocity anisotropy upon entering the C phase from above. This and other features will be discussed elsewhere.[21]

To conclude, we have observed, for the first time, an anomalous attenuation and velocity dispersion of longitudinal ultrasound near an A-C phase transition. The anomaly is found to be strongly anisotropic. Furthermore, no effect due to critical fluctuations above T_{AC} is observed, in strong contrast with other liquid-crystal transitions. The results are consistent with a mean-field dynamics of the Landau-Khalatnikov type: The anomaly is due to the relaxation of the bulk order parameter. This result strongly supports the view that the A-C transition, in this material at least, is of the mean-field type. The superconducting transition is the only other case in a bulk system, to the best of our knowledge, where the mean-field dynamics holds.[22] More experimental work, perferably in systems with a wide smectic-A range, would be desirable.

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